

# Chemical Speciation of Sulfur in Marine Cloud Droplets and Particles

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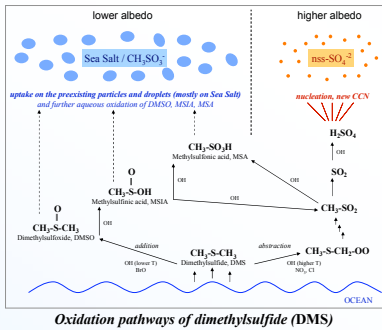
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## ABSTRACT

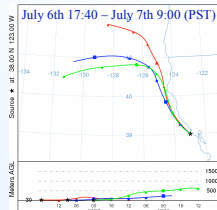
Chemical speciation and apportionment of sulfur containing compounds in individual marine particles is facilitated by a complementary combination of time-of-flight secondary ionization mass spectrometry (TOF-SIMS), computer controlled scanning electron microscopy with energy dispersed analysis of X-rays (CCSEM/EDX) and scanning transmission X-ray microscopy (STXM) with near edge X-ray absorption fine structure spectroscopy (NEXAFS). Chemical speciation of sulfur provides important insights into the atmospheric chemistry of marine particles collected in the field study at Pt. Reyes National Seashore. The obtained results indicate separate formation of methylsulfonic acid (MSA) in cloud droplets and ammonium sulfate in smaller particles. These observations are indicative of two different pathways in the multiphase oxidation chemistry of dimethyl sulfide (DMS) in the marine boundary layer which are consistent with recent modeling study of von Glasow and Crutzen (2004).

## INTRODUCTION

The most important gaseous precursor for sulfate aerosol over the oceans is dimethyl sulfide (CH<sub>3</sub>SCH<sub>3</sub>/DMS), which is produced by phytoplankton and subsequently emitted to the atmosphere where it is oxidized *via* two main reaction pathways: addition of an O atom and abstraction of an H atom. The major DMS oxidation products include sulfur dioxide (SO<sub>2</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), dimethylsulfoxide (CH<sub>3</sub>SOCH<sub>3</sub>/DMSO), methanesulfonic acid (CH<sub>3</sub>S(O)OH/MSA), methanesulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H/MSA) in addition to some other species. Under atmospheric conditions, H<sub>2</sub>SO<sub>4</sub> is the only product of the DMS oxidation that can form new aerosol particles (new CCN). All other products condense onto existing particles, increasing the particle diameter. The partitioning between H<sub>2</sub>SO<sub>4</sub> and other DMS oxidation products is important because increasing the number of particles and increasing particle size can impact climate related properties of aerosols and cloud droplets differently, i.e. scattering and absorption of sunlight (direct effect) as well as changing the microphysical structure, lifetime, and amount of clouds (indirect effects).



## LOCATION OF FIELD MISSION: Pt. Reyes California, July 2005



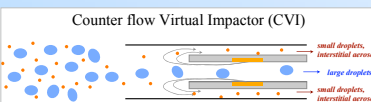
### Location of the sampling site

### Low altitude clouds

### Air mass from ocean

North California coast is an area of phytoplankton bloom - high concentrations of reactants for oxidation of DMS.  
Frequent low altitude clouds - existing particles for DMS oxidation products to condense on.  
Cold Ocean surface - low temperatures promote radical addition reactions.

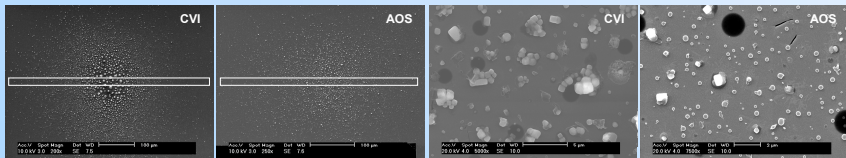
High CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>/nss-SO<sub>4</sub><sup>2-</sup> ratios are expected in individual sea salt particles according to a number modeling studies!



Schematics of Counter flow Virtual Impactor.

Time resolved sampling was conducted at time intervals of 12 min. Cloud droplets and interstitial aerosol have been separated using the Counter flow Virtual Impactor (CVI) (Ogren *et al.*, 1985). CVI - sampling of cloud droplets (> 5 μm) followed by evaporation of these droplets enabling study of the residual aerosol particles. AOS - sampling of < 5 μm particles in the fog (interstitial aerosol).

## RESULTS AND DISCUSSION



Low magnification SEM images of CVI and AOS samples.

High magnification SEM images of CVI and AOS samples.

Low magnification SEM images of CVI and AOS samples indicating the spatial inhomogeneity of the deposition. The CVI samples consist of larger particles than the AOS samples. In addition, larger particles tend to be in the center of the impact region with smaller particles located closer to the periphery.

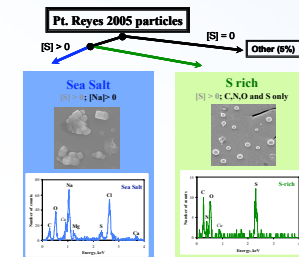
Fragments of CVI and AOS samples (central areas of the samples) shown at higher magnifications. Sea salt particles (those with NaCl crystals) are abundant in CVI samples, round particles are more abundant in AOS samples.

**References:** Von Glasow and Crutzen (2004), *ACP*, 4, 589-608; Ogren *et al.* (1985), *GRL*, 12, 121-124

## • CCSEM/EDX Analysis

A total of 12 samples (6 CVI and 6 AOS) taken at even time intervals from the period of July 6th 17:40 – July 7th 9:00 (PST) were analyzed by CCSEM/EDX (~1000 particles per sample, 14000 particles total).

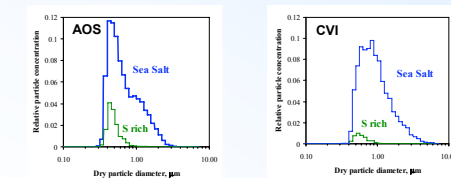
An assignment of individual particles into three broad classes has been applied based on their elemental composition measured by the EDX.



**Sea salt** – particles that contained Na, Mg and S.

**S-rich** – particles that contained only S and low-Z elements.

Others – all particles with no S were assigned to this class (less than 5% by number in all the samples)



Size distributions of Sea Salt and S-rich particles measured by CCSEM/EDX in AOS and CVI samples.

The two size distributions plotted in each of the panels are normalized to the total number of particles analyzed in CVI and AOS samples, respectively. The sea salt particles have a wider size range and contribute significantly to both CVI and AOS samples. The S-rich particles are smaller and have a narrow size distribution. As expected, they are more abundant in the AOS sample.

Mass balance assuming 1/2 Cl deficit is from sulfate formation  
2NaCl + H<sub>2</sub>SO<sub>4</sub> → Na<sub>2</sub>SO<sub>4</sub> + 2HCl(g)

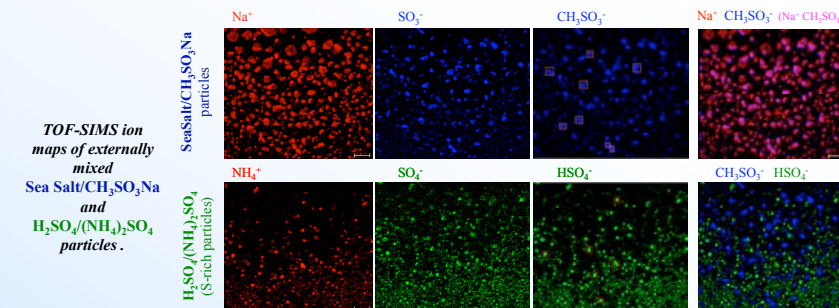
CCSEM/EDX data indicates Cl depletion in the sea salt particles and non-sea salt sulfur (nss-S) enrichment. The mass balance of C/Na, (Cl+0.5×S)/Na, and (Cl+S)/Na atomic ratios presented in figures on the left point out the likelihood of CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> as a major form of nss-sulfur present in sea salt particles!

Mass balance assuming Cl deficit is from formation of methanesulfonate only  
NaCl + CH<sub>3</sub>SO<sub>3</sub>H → CH<sub>3</sub>SO<sub>3</sub>Na + HCl(g)

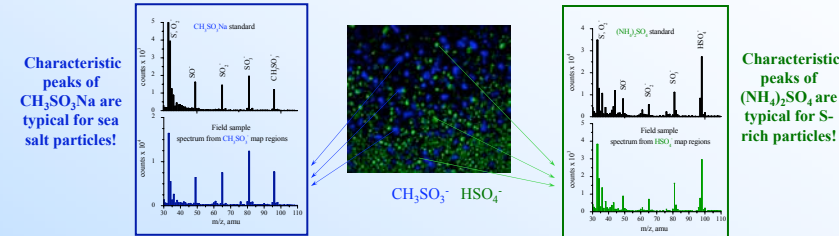
Comparison of the (Cl+S)/Na and the (Cl+S+N)/Na ratios indicate that significant nitrate (NaNO<sub>3</sub>) is not present in particles.

## • TOF-SIMS Analysis

Ion maps shown below indicate two different, externally mixed types of particles: Sea salt/CH<sub>3</sub>SO<sub>3</sub>Na (larger particles) and H<sub>2</sub>SO<sub>4</sub>/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (smaller particles).

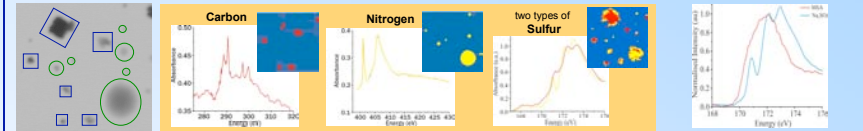


In order to confirm the molecular composition of sulfur in these particles, spectra taken from regions of interest (marked with red squares) were compared with those from laboratory standards of CH<sub>3</sub>SO<sub>3</sub>Na and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> as illustrated below.

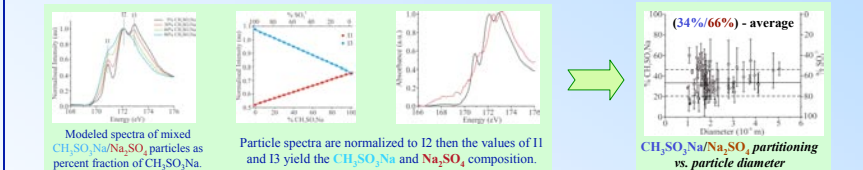


## • STXM/NEXAFS Analysis

STXM/NEXAFS is used to study chemical bonding information of different elements for individual particles. This enables the speciation of different components with the aim of quantifying CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>/SO<sub>4</sub><sup>2-</sup> ratios in individual particles. Figures below show a STXM image and maps generated by principle component analysis of a region containing two particle types.



STXM/NEXAFS image and elemental maps of Sea Salt/CH<sub>3</sub>SO<sub>3</sub>Na and H<sub>2</sub>SO<sub>4</sub>/(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles.



## • Combined use of STXM/NEXAFS and CCSEM/EDX data to determine CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>/nss-SO<sub>4</sub><sup>2-</sup> ratios in sea salt particles

CCSEM/EDX analysis:

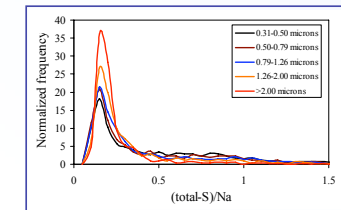
$$\frac{[\text{total-S}]}{[\text{Na}]} = \frac{[\text{nss-SO}_4^{2-}]}{[\text{Na}]} + \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{Na}]} + \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{Na}]} = 0.06 + \frac{[\text{nss-SO}_4^{2-}]}{[\text{Na}]} + \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{Na}]}$$

STXM/NEXAFS analysis:

$$\frac{[\text{CH}_3\text{SO}_3^-]}{[\text{total-SO}_4^{2-}]} = \frac{[\text{CH}_3\text{SO}_3^-]/[\text{Na}]}{[\text{nss-SO}_4^{2-}]/[\text{Na}] + [\text{CH}_3\text{SO}_3^-]/[\text{Na}]} = \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{SO}_4^{2-}]_{\text{nss}}}$$

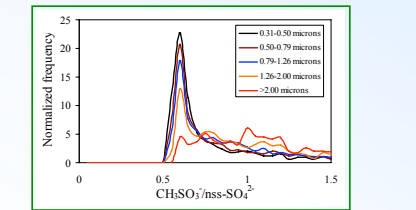
CCSEM/EDX analysis provides values of [total-S]/[Na] measured in individual particles. STXM/NEXAFS provide values of [CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>]/[total-SO<sub>4</sub><sup>2-</sup>] measured in individual particles. The two data sets are combined, using the equations depicted on the left, to yield values of [CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>]/[nss-SO<sub>4</sub><sup>2-</sup>] as a function of particle size.

### • total-S/Na ratios are higher for smaller particles!



Distributions of total-S/Na ratios detected in individual particles plotted for different size bins (CCSEM/EDX data)

### • CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>/nss-SO<sub>4</sub><sup>2-</sup> ratios are higher for larger particles!



Distribution of CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>/nss-SO<sub>4</sub><sup>2-</sup> ratios derived for individual particles plotted for different size bins: (combined CCSEM/EDX and STXM/NEXAFS data)

## CONCLUSIONS

• Unambiguous, quantitative assessment of CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>/nss-SO<sub>4</sub><sup>2-</sup> ratios in individual sea salt particles has been facilitated using combined data from three techniques.

- CCSEM/EDX – quantitative assessment of elemental composition of individual particles
- TOF-SIMS – qualitative molecular speciation of S-containing compounds in individual particles
- STXM/NEXAFS – quantitative assessment of CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> vs. SO<sub>4</sub><sup>2-</sup> within individual particles

### • Specific findings:

- Particle size specific data on nss-S/Na and CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>/nss-SO<sub>4</sub><sup>2-</sup> ratios are reported for residues of marine cloud droplets
- Characteristic ratios of nss-S/Na > 0.10 are reported for sea salt particles with higher values for small particles. Extensive formation of S-containing salts and Cl depletion in small particles.
- Characteristic ratios of CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>/nss-SO<sub>4</sub><sup>2-</sup> > 0.70 are reported for sea salt particles with higher values for large particles. Higher capacity for CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> (lower conversion to SO<sub>4</sub><sup>2-</sup>) is reported for large particles

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